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New Syntheses of Intermediates in the German Chemical Industry

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During the past three years a mass of information has been accumulated on the later developments in the German chemical industry. This information is contained in a very large number of reports written by our technical investigators and in microfilms taken from the original German sources, all of which is being cleared through the Office of Technical Services of the Department of Commerce. In addition, there have appeared many articles of a review nature in the current chemical journals.

Some of the most interesting developments were in the field of organic intermediates. There were carried to the commercial stage new syntheses of many aliphatic chemicals of great importance as starting materials for synthetic rubbers, plastics, and fibers. Lower costs resulted from the use of cheaper raw materials and development of newer and simpler processes. It may be of value to list some of the more important related syntheses belonging to this category.

In most of the new reactions unsaturated hydrocarbons, notably acetylene and olefins, were employed as building blocks. Reactions were usually carried out under pressure and in the presence of catalysts. Dr. Walter Reppe at I. G. Farbenindustrie, A-G, in Ludwigshafen developed an entirely new chemistry built around acetylene, and extended some of the reactions to the olefins.

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Vinyl Ethers

Reppe's earliest work, initiated about 1932, was on the synthesis of vinyl ethers from alcohols and acetylene by employing the so-called "vinylation" reaction. The type reaction for aliphatic alcohols was:

$$ROH + C_2H_2 \longrightarrow ROCH{=}CH_2.$$

With the lower alcohols such as methyl and ethyl, 5 to 10 per cent of KOH was dissolved in the alcohol and the reaction was carried out at 170°-180°C under pressures of 15-20 atmospheres with a compressed mixture of acetylene containing about 50 per cent of inert gas such as nitrogen. With the alcohols boiling at or above the reaction temperature, no pressure was required. The "vinylation" reaction is interesting as an intermediate step in the conversion of acetylene to acetaldehyde, since the vinyl ether is readily hydrolyzed to acetaldehyde, re-forming the alcohol.

Acrylates

A new direct route for the synthesis of acrylates was developed by Reppe in which acetylene was combined directly with carbon monoxide. This type of reac-

tion is called "carbonylation." The reaction is carried out in an alcohol solution, yielding the ester in accordance with the equation:

$$ROH + C_2H_2 + CO \longrightarrow CH_2{=}CHCO_2R.$$

The alcohol containing a few per cent of nickel bromide catalyst flows through a packed column maintained at a temperature of 160°-180°C and at a pressure of 30 atmospheres. A 50-50 mixture of carbon monoxide and acetylene is compressed into the column and a 30 to 50 per cent solution of the acrylic ester is withdrawn from the bottom of the column. The catalyst can be reused many times before regeneration.

Acrylonitrile

The direct synthesis of acrylonitrile was being developed during the latter stages of the war at the I. G. Farben plants of Ludwigshafen, Huels, and Leverkusen. At Leverkusen a commercial unit was in operation. The catalyst for this reaction was a modified Nieuwland catalyst, such as was developed for vinyl acetylene. Acetylene was reacted with hydrogen cyanide,

$$C_2H_2 + HCN \longrightarrow CH_2{=}CHCN.$$

The mixture of gases was passed through the liquid catalyst at 80°-100°C and at atmospheric pressure.

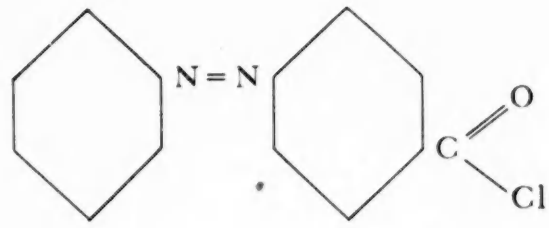
In connection with the work on the new acrylonitrile process, there was developed at Oppau a new method of producing HCN in accordance with the following equations:

$$CH_3OH + CO \longrightarrow HCO_2CH_3$$
$$HCO_2CH_3 + NH_3 \longrightarrow HCONH_2$$
$$HCONH_2 \longrightarrow HCN + H_2O.$$

The first step was carried out in an autoclave using one per cent NaOH as catalyst at a temperature of 100°-110°C and a pressure of 200 atmospheres. The methyl formate was then reacted with ammonia in an autoclave at 10-15 atmospheres. The resulting formamide was pyrolyzed over an alumina catalyst at 250°C to yield HCN. Over-all yield for the process was about 80 per cent.

This article will be concluded in the next issue of the *Bulletin*. None of the statements made should be considered as recommendations for the use of this information in violation of any patents now in force, or which may be issued in the future. It is assumed that anyone making use of any of the information contained herein will make the usual patent investigations.

p-Phenylazobenzoyl Chloride, Versatile Reagent



A compound with interesting possibilities in the field of natural products, especially sterols, is p-phenylazobenzoyl chloride*. It has been used by K. Ladenburg, E. Fernholz, and E. S. Wallis, for the chromatographic separation of sterols [*J. Org. Chem.*, 3, 294-9 (1938)].

Esters are formed by heating the reagent with the hydroxy compounds in pyridine for an hour at 100°C. They may be precipitated with methanol and crystallized from benzene. Mixtures of these colored esters can be developed on alumina and separated by means of the variation in tints.

An additional useful characteristic of p-phenylazobenzoyl chloride is its tendency to form from complex alcohols readily crystallizable esters having sharp melting points.

*Eastman Organic Chemical No. 5549.

Erratum

Volume 20, No. 3, page 1 (1948)

In the article "Telomers" by Dr. J. A. VanAllan, the reaction product of octene-1 and trichlorosilane should have read: $CH_3(CH_2)_5CH_2CH_2SiCl_3$.

Better Delivery of Eastman Organic Chemicals

NEW facilities for the production of Eastman Organic Chemicals are now in operation. This is expected to improve deliveries of the laboratory and research compounds which the Eastman Kodak Company supplies to chemists of the United States and of many other lands.

The new laboratory building just completed is the first of three units planned by the company to aid in meeting greatly increased demands of research workers for organic chemicals. Completion of the second unit, now under construction, is expected in 1949. A third will be erected later.

The construction is on the site of the original laboratory buildings, put up in 1918 in a non-profit emergency program to provide chemicals for scientific workers whose German sources of supply were cut off by World War I blockade. The list of 150 chemicals offered at that time has now lengthened to more than 3,000, constituting the world's most complete stock of organic chemicals.

The building just finished contains nine unit laboratories, designed for manipulative efficiency in the syntheses and purifications that are performed in relatively small quantity. A special jet injector pump provides 250 gallons of water a minute to the fume-eliminating air-conditioning system. The glazed tile walls have border joints which permit them to be washed down with solvents or strong acids. Shatterproof glass shields permit the chemists to work in safety while watching and controlling the synthesis of certain compounds.

The improved facilities not only provide better working conditions for the present staff of skilled chemists, but will make physically possible an increase in the professional staff. This is essential to boost production capacity for the chemicals now listed, and to synthesize entirely new chemicals.

Some Eastman Organic Chemicals are industrial chemicals, packaged in convenient quantities to save research workers the trouble of locating materials among diverse commercial sources of supply. As industrial conditions have changed, some of these compounds from time to time have dropped from the market and have therefore been removed from the Eastman list. It is hoped that the new production facilities will permit restoration to the Eastman catalog of many of these discontinued items.

New Eastman Organic Chemicals

5952 3-Amino-1,2-dimethylbenzene Hydrochloride....100 g. .. $3.50 C
$NH_2C_6H_3(CH_3)_2 \cdot HCl$ . . . MW 157.64

P 5980 Cyclohexaneacetic Acid (Pract.) MP 28-29°.....500 g. .. 8.00 D
$CH_2(CH_2)_4CHCH_2COOH$ . . . MW 142.19

P 5981 Cyclohexanebutyric Acid (Pract.) MP 30-31°....500 g. .. 7.00 D
$CH_2(CH_2)_4CH(CH_2)_3COOH$ . . . MW 170.24

P 5982 Cyclohexanecaproic Acid (Pract.) MP 31-33°....500 g. .. 7.00 D
$CH_2(CH_2)_4CH(CH_2)_5COOH$ . . . MW 198.30

P 5978 Cyclohexanepropionic Acid (Pract.) MP 16-18°..500 g. .. 8.50 D
$CH_2(CH_2)_4CHCH_2CH_2COOH$ . . . MW 156.22

P 5979 Cyclohexanevaleric Acid (Pract.) MP 16-18°....500 g. .. 8.00 D
$CH_2(CH_2)_4CH(CH_2)_4COOH$ . . . MW 184.27

5524 2,6-Dinitro-4-chloroaniline MP 145-147°.....100 g. .. 4.00 C
$(NO_2)_2C_6H_2ClNH_2$ . . . MW 217.57

P 5950 Ethylenethiourea (Pract.) MP 198-200°.....500 g. .. 3.25 D
$CH_2CH_2NHCSNH$ . . . MW 102.16

5946 Ethyl Hydantoate MP 135-137°.....100 g. .. 9.00 C
$NH_2CONHCH_2COOC_2H_5$ . . . MW 146.15

5971 2-Methyltetrahydrofuran BP 78-79°.....500 g. .. 7.00 D
$OCH_2CH_2CH_2CHCH_3$ . . . MW 86.13

P 5975 iso-Propyl N-Phenylcarbamate (Pract.)
MP 85-88°.....500 g. .. 6.00 D
$C_6H_5NHCOOCH(CH_3)_2$ . . . MW 179.21

5897 Sodium Diphenylaminesulfonate..... 10 g. .. 6.00 A
$C_6H_5NHC_6H_4\text{-}4\text{-}SO_3Na$ . . . MW 271.27

P 5977 Thiazole Yellow GGM, Extra Concentrated
(For Magnesium Determination) (Pract.)... 10 g. .. 1.50 A
$[SC_6H_3\text{-}6\text{-}(CH_3)N{:}C\text{-}4\text{-}C_6H_3\text{-}2\text{-}SO_3Na\text{-}1\text{-}]_2N{:}NNH$- . . . CI 813

P 5961 2,3,5-Trimethylphenol (Pract.) MP 94-96°.....100 g. .. 5.00 C
$(CH_3)_3C_6H_2OH$ . . . MW 136.19

P 5868 s-Trioxane (Pract.) MP 61-63°..... 1 kg... 3.45 E
$OCH_2OCH_2OCH_2$ . . . MW 90.08

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